Magnetism of CaV_2O_5, CaV_3O_7, CaV_4O_9: quantum effects or orbital ordering?

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Abstract

The quasi 2-d spin $\frac{1}{2}$ materials CaV_nO_{2n+1} (n=2,3,4) are often treated as systems in which quantum effects play a dominant role: CaV_2O_5 has a spin gap and is thought to be a spin ladder; CaV_3O_7 has unusual long-range magnetic order which is explained by quantum fluctuations; the spin gap in CaV_4O_9 is usually attributed to the formation of plaquette RVB. We show that in all these compounds there should exist an orbital ordering which strongly modifies the exchange interaction and provides an alternative explanation of their magnetic properties, without invoking special quantum effects. The type of magnetic ordering obtained for CaV_3O_7 quite naturally explains its magnetic structure which turns out to be that of a quasi 1-d antiferromagnet. The structure of CaV_4O_9 corresponds to singlet dimers rather than to a plaquette RVB. Singlet dimers should exist also in CaV_2O_5. The chirality of the crystal structure of CaV_4O_9 is also mentioned and some possible consequences are briefly discussed.

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Low dimensional magnetic materials attract now considerable attention. Particularly interesting are the systems with a marked quantum behaviour, having singlet ground states with spin gaps (materials with spin-Peierls transitions, spin-ladders, layered cuprates etc.). Most of such systems studied up to now contain Cu^{2+} ions, which have one hole in the d-shell and consequently spin $\frac{1}{2}$. Recently a new class of V compounds (CaV_nO_{2n+1}, n=2,3,4) was found with rather unusual magnetic properties, mostly ascribed to quantum effects. They contain V^{4+} ions with one d-electron, so that they are often treated as electron counterparts of the cuprates. The first member of this family, CaV_2O_5, was found to have a spin gap and is considered as a spin ladder [1]. The second one, CaV_3O_7, has long range antiferromagnetic ordering at $T_N \simeq 23$ K with an unusual magnetic structure [2]. Quasiclassical treatment of the Heisenberg model was not able to reproduce this structure, which stimulated the authors of Ref. [3] to invoke quantum fluctuations in order to explain it. And, last but not least, CaV_4O_9 was the first of these systems to attract considerable attention. Immediately after the first experimental paper [4], there was a burst of theoretical activity around this compound [5], which was treated as the first example of a new situation, the so called plaquette RVB — a singlet state on 4 sites of a plaquette. This is of course a very exciting development. We want to point out, however, that the actual situation in the system CaV_nO_{2n+1} may be quite different from what was discussed in Refs. [1]- [5]: the orbital degrees of freedom, completely ignored up to now, play here a crucial role and provide a different explanation of the observed phenomena. In the previous treatments [1]- [5] one proceeded from the homogeneus Heisenberg interaction. In this model, the orbital character of the electronic wave function is ignored, and the exchange interaction is taken as isotropic. However, if ions with degenerate orbital configurations are present, according to Jahn-Teller theorem the degeneracy must be lifted in the ground state: a particular orbital is stabilized at each site, making the exchange interaction inhomogeneus. This orbital ordering (cf. [6]) gives a very simple explanation of the magnetic properties of CaV_nO_{2n+1}, without invoking special quantum effects.

The fundamental structural unit of the CaV_nO_{2n+1} compounds is a VO_5 pyramid with a

square base, containing the V ion slightly shifted from the basal plane. Alternated up and down pyramids line up, with their square bases sharing common edges and forming 2-d V-O sheets; Ca ions are located between these sheets. In different members of this family, certain V ions are missing in a regular fashion, so that we can describe the CaV_nO_{2n+1} series by a 2-d square lattice with every third, fourth or fifth ion missing. In a square pyramid coordination, d-states are split into a ground state doublet (d_{xz}, d_{yz}), and a higher energy singlet d_{xy}; this is confirmed by ESR (Taniguchi et al, cited in [2]). The d-electron of V^{4+} occupies at each site one of these degenerate states or their linear combination: $|\alpha> = \cos\alpha|d_{xz}> + \sin\alpha|d_{yz}>$, where the angle α gives the orientation of the plane in which the orbital lies with respect to the x-axis. We will show that the crystal structure selects the value of α, leading in each compound to certain orbital ordering. The simple consideration that, due to this selective occupation of orbitals, each V has different exchange coupling with different neighbours, explains the failure of an approach which uses an uniform Heisenberg interaction. With the proper orbital ordering, the magnetic behaviour is straighforwardly determined by the Goodenough-Kanamori-Anderson (GKA) rules [7], and the appeal to subtle quantum effects becomes unnecessary.

We start with CaV_3O_7, which turns out to be the simplest and clearest case. The basic elements of its crystal structure are shown in fig.1 together with the orbital ordering obtained in [2]. The attempts to reproduce it on the basis of the homogeneus Heisenberg interaction in a mean field approximation failed for any values of the nn exchange J_e (across the edges of plaquettes) and nnn exchange J_c (across the corners) [3]. As a possible way out, the inclusion of quantum fluctuations was suggested in [3], but agreement with the experimental magnetic structure was found only in a narrow range of parameters. We show now that this magnetic structure is a natural consequence of the orbital ordering which should exist in this compound. Two kinds of V sites are present in this lattice: the one symmetrically surrounded by two nn V ions and two nn empty plaquettes (site A), and the one with three nn V ions and one nn empty plaquette (sites B, B', C). The d-electron at a site A obviously prefers to occupy an orbital pointing towards the two positive charges in B and B', i.e. there

should exist an extra crystal field splitting of the d_{xz} and d_{yz} orbitals stabilizing the d_{xz}. For the same reasons, the d_{yz} orbital will be occupied at site B, B',C . To check these arguments we carried out simple calculations treating the crystal field in a point charge model. For the site A and in a nn approach, the electrostatic energy splitting we are interested in is given by

$$\Delta_{\mathrm{CF}} = 2 \int \frac{-4\,e^2 \left(|\psi_{\mathrm{yz}}(\mathbf{r}')|^2 - |\psi_{\mathrm{xz}}(\mathbf{r}')|^2 \right)\, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \tag{1}$$

where $\mathbf{r}$ and $\mathbf{r}'$ are the positions of the V^{4+} ion in B (or B') and of the d-electron respectively. A standard expansion of the 1/r point charge potential in spherical harmonics shows that only the quadrupole terms contribute, giving

$$\Delta_{\mathrm{CF}} = (\mathbf{Q}_{\mathrm{dxz}} - \mathbf{Q}_{\mathrm{dyz}})\cdot\nabla\mathbf{E}_{\mathrm{CF}} \tag{2}$$

(contraction of the quadrupole tensor of the d orbitals $\mathbf{Q}$, and the electric field gradient (EFG) tensor $\nabla\mathbf{E}_{\mathrm{CF}}$ created at the V site by the point-charge neighbours). The tensor $(\mathbf{Q}_{\mathrm{dxz}} - \mathbf{Q}_{\mathrm{dyz}})$ is traceless and diagonal, its xx component being $q=9.15\cdot10^{-28}$ in cgs units, while the zz one is zero for symmetry reasons. We then proceed by calculating and diagonalizing the EFG tensor, whose principal axes fix a new frame of reference $x'y'z'$ in which the expression for the splitting becomes $\Delta_{\mathrm{CF}}=q\cdot(\nabla\mathbf{E}_{\mathrm{CF}}^{x'x'} - \nabla\mathbf{E}_{\mathrm{CF}}^{y'y'})$ and the occupied orbital is $d_{x'z'}$ or $d_{y'z'}$ according to the sign of Δ_{CF}. The resulting splitting at site A is $\Delta_{CF} \simeq 0.36$ eV, the d_{xz} orbital being the lowest one. In a more detailed treatment with 20 neighbours $\Delta_{CF} \simeq 0.33$ eV. Covalency contributions to the splitting play here a minor role because the t_{2g} orbitals do not point towards the oxygen ligands, and they have been neglected. A more subtle point to consider is the out of plane position of the V ions with respect to the oxygen lattice. According to structural data [9,10], the angle between the V-basal oxygen line and the basal plane is about 25° in all the CaV_nO_{2n+1} compounds. If this is taken into account in the EFG tensor, for the 20 neighbours cluster the splitting is reduced to about 0.31 eV, which is still large enough to support our idea: up to reasonable temperatures, only the d_{xz} orbital is occupied at site A. Similar treatment shows that the d_{yz} orbital is stabilized

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at site B, B' and C, with the stabilization energy $\Delta_{CF}(B)=0.5\ \Delta_{CF}(A)$, in agreement with the symmetry considerations. The conclusion is that, simply due to the crystal structure, there exists in CaV_3O_7 the orbital ordering represented in fig.1, where the projection of the occupied orbitals on the basal plane is shown. This ordering should be accompanied by an average elongation of plaquettes along the y direction, which actually has been detected [9].

From the GKA rules [7] it is then evident that there will be strong antiferromagnetic exchange along the y-direction, whereas in the x-direction the interaction will be ferromagnetic and much weaker. (Although nn V-O-V coupling along the antiferromagnetic chain is a 90° one, it is antiferromagnetic because we are dealing with the π-bonding of d_{yz} orbitals). This quite naturally explains the magnetic structure of fig.1. The nnn interaction across the corners of the plaquettes, namely between sites A and C, will be antiferromagnetic too, once more supporting the long range magnetic order experimentally observed. With this type of orbital ordering one can visualize the magnetic properties of CaV_3O_7 as those of weakly coupled 1-d antiferromagnetic chains parallel to the y-axis (in this respect CaV_3O_7 is analogous to $KCuF_3$, which is a very good quasi 1-d antiferromagnet due to a particular type of orbital ordering [6]). This conclusion finds support in the behaviour of the magnetic susceptibility [2], which, as typical for quasi 1-d antiferromagnets, has a pronounced maximum at $T_{max} \simeq 95$ K, much higher than $T_N \simeq 23$ K. We checked that the whole $\chi(T)$ curve can be fitted rather well by the Bonner-Fisher expression [12] for temperatures above 35 K. The standard treatment [12] gives that the exchange integral along the chain is $J_{1d} \simeq T_{max}/0.64 \simeq 150$ K. Weaker interactions between the chains give 3-d ordering at much lower temperature ($T_N \simeq 23$ K).

We turn now to the most interesting case, CaV_4O_9. The spin gap observed in [4] was generally attributed to plaquette RVB [5], but we show that the inclusion of orbital degrees of freedom again drastically modifies the situation. The schematic elements of the crystal structure of this compound [9] are shown in fig.2. (This structure is rather interesting in itself: one can visualize it as the trace of the walk of the "left-moving knight" on a chessboard. Of course the right-hand variant exists as well. Correspondingly, each plane has

certain chirality, and the whole sample may be chiral too, displaying for example an optical activity and many other interesting properties). In CaV_4O_9 every V ion has the same surrounding, i.e. just one kind of site exists in which the electric field is rather asymmetric. As far as the 4 nn plaquettes of a V ion are concerned, the situation is the same as at site B in CaV_3O_7 (fig.1): at this level we expect the occupied orbital at each V site to be d_{xz} or d_{yz} — namely the one parallel to the edge of the nn empty plaquette. The inclusion of more distant neighbours leads to a tilting of the principal axes of the EFG tensor, and consequently of the occupied orbital, from the x and y directions; however, for a cluster with 20 empty plaquettes, we obtained just a small tilting angle $\alpha \simeq 9°$ (see fig.2), the stabilization energy being $\Delta_{CF} \simeq 0.18$ eV. With this orbital structure the strongest antiferromagnetic interaction is that within dimers shown in fig.2, the next one is J_{corner}, while the edge exchange between dimers is weaker and ferromagnetic. We thus expect the 2-d lattice to be covered by singlet dimers with, because of the tilting, J_{dimers} somewhat smaller than $J_{1d}(\simeq 150$ K$)$ estimated above for CaV_3O_7, in agreement with the observed spin gap of 107 K [4]. These dimers can be additionally stabilized by the outward shifts of the V ions away from the points marked in fig.2 by triangles (the centers of the V plaquettes in the "plaquette RVB" picture): it should be caused both by the electric field, which we calculated to be about 1.1 10^6 in cgs units along the arrows at each V site, and by the dimer energy gain itself. These shifts are indeed experimentally observed in [11]; note that they are opposite to those suggested by Starykh et al [5] within the plaquette RVB picture.

Finally we discuss the situation in CaV_2O_5 (fig.3), which turns out to be somewhat more delicate. The first striking feature of this compound, usually treated as a spin ladder [1], is the large value of the spin gap $\Delta_{SG}=616$ K, even larger than in copper ladders (typically $\sim$400 K [14]). If we assume relatively isotropic interactions with $J_{rung} \simeq J_{leg}$, we would need $J \geq 1200$ K [14], i.e. of the same order as in High-T_C cuprates. But in contrast to the Cu^{2+} case, for V^{4+} we are dealing not with e_g but with t_{2g} electrons, and their much smaller overlap with the oxygen ligands should give a weaker exchange. We show below that the possible solution of this puzzle lies again in the orbital ordering with the concomitant shift

of the V ions and with the formation of tightly bound rung dimers. The calculation of the EFG tensor at the centre of each oxygen plaquette, where the V ions are supposed to be, shows that the orbital $d_{x'z}$, tilted by $45°$ with respect to the original x axis, would be there more stable. However, the stabilization energy is in this case only $\Delta_{CF} \simeq 0.06$ eV. With this type of orbital occupation, the large value of the spin gap [1] could hardly be explained, and no gap might exist at all. Straightforward calculation shows, however, that in the centre of the oxygen plaquettes there exists strong electric field along the rungs ($2.1 \cdot 10^6$ in cgs units). Consequently, we expect a shift of the V ions in the direction of the arrows in fig.3, which shortens the V-V distances in the rungs. If this shift δ is taken into account in the calculation of the EFG tensor, the splitting Δ_{CF} changes sign for $\delta > \delta_C \simeq 0.2\mathring{A}$. For larger shifts the different orbital, $d_{y'z}$, lies lower in energy, its stabilization energy rapidly increasing with δ: the resulting orbital ordering is shown in fig.3. Such a structure can explain the experimental observations: we would have here a strong A-A' interaction ($180°\pi$-bonding), and much weaker A-B and A-C interactions, so that the picture would again predominantly correspond to weakly coupled dimers. Note that here $J_{AB} < J_{AC}$, and the ladder model is thus completely inapplicable. In order to explain the spin gap of 616 K [1], we need in this framework J_{dimer} of the same order, i.e. ~ 4 times stronger than the ~ 150 K we estimated for CaV_3O_7. Several factors actually strenghten this interaction: the in-plane shift of the V ions decreases the V-V and V-bridging oxygen distances enhancing the overlap; moreover, we have here $180°$-exchange in contrast to the weaker $90°$-exchange in chains in CaV_3O_7 and in dimers in CaV_4O_9 (note however that there are two oxygens contributing to the exchange in the latter cases). The main factor however is the out of plane position of the V ions. This leads to an extra contribution to the exchange due not only to π- but also to σ-overlap (fig.4), which depends on the angle γ between the direction V-planar oxygen and the basal plane, $\tilde{t}_{pd\sigma} = t_{pd\sigma} cos\gamma \sin(2\gamma)$. The d-p σ hybridization $t_{pd\sigma}$ is typically ~ 2 times stronger than the π one [8]. As the exchange interaction $J \sim t_{pd}^4$, σ-hybridization gives significant contribution even for small γ, being much smaller for $90°$-exchange in CaV_3O_7 (where it is also present) due to partial cancellation of different terms. Combining all the

contributions to the exchange, we get for the real structure ($\gamma \simeq 25°$) that the total interaction in dimers in CaV_2O_5 is about three times stronger than in chains of CaV_3O_7 even without taking into account shifts of the V ions. Thus this orbital ordering can explain the properties of CaV_2O_5, although more detailed experiments and calculations are needed to check the proposed picture. Summarizing, we have shown that the properties of the system CaV_nO_{2n+1}, often treated as electron counterpart of the Cu compounds, can be easily understood with the orbital degrees of freedom taken into account: an orbital ordering should exist in these vanadates, which drastically modifies their exchange interactions and strongly influences their magnetic properties. The type of ordering obtained for CaV_3O_7 makes it a quasi 1-d antiferromagnet and quite naturally explains its unusual magnetic structure, without the necessity to invoke complicated quantum effects. Ordinary spin singlet dimers should be formed in CaV_4O_9 as a result of the orbital ordering, instead of the plaquette RVB previously assumed. The most natural explanation of the properties of CaV_2O_5 with its unexpectedly large spin gap is the formation of tightly bound dimers due to V ions shift and corresponding orbital ordering. Thus, the materials of the series CaV_nO_{2n+1} provide yet another example of how the orbital structure of transition metal compounds [7,6,13] often makes the homogeneus Heisenberg exchange inapplicable, giving rise to peculiar magnetic structures and nontrivial magnetic properties. Finally, we point out that the crystal structure of CaV_4O_9 is chiral. To our knowledge, this is the first example of structurally chiral magnetic material. The unique combination of this chirality (and corresponding spontaneus optical activity) with the presence of localized magnetic moments, opens a broad spectrum of new possibilities and can lead to interesting physical consequences, e.g. in magnetooptical properties etc.

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FIGURES

FIG. 1. CaV_3O_7: crystal and magnetic structure. Oxygen ions are at the corners of the plaquettes, and V ions in the center. Orbital ordering is also shown (see the text).

FIG. 2. CaV_4O_9: crystal structure and orbital ordering. Singlet dimers are marked by dashed ovals.

FIG. 3. CaV_2O_5: crystal structure and possible orbital ordering. The usual "ladder" is shown.

FIG. 4. CaV_2O_5: the extra σ-overlap.